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LEACHING OF TCIPP FROM FURNITURE FOAM IS RAPID AND SUBSTANTIAL

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Abstract

A series of laboratory experiments were conducted, in which waste furniture polyurethane foam samples containing tris (1-chloro-2-propyl) phosphate (TCIPP) were contacted with a range of leaching fluids, formulated to simulate the composition of landfill leachate. Leaching was examined under a number of different scenarios, such as: dissolved humic matter concentration, pH, and temperature, as well as the effect of agitation, and waste:leaching fluid contact duration. In addition to single batch (no replenishment of leaching fluid), serial batch (draining of leachate and replenishment with fresh leaching fluid at various time intervals) experiments were conducted. Leaching of TCIPP from PUF appears to be a first order process. Concentrations of TCIPP in leachate generated by the experiments in this study ranged from 13 mg L^{-1} – 130 mg L^{-1} . In serial batch leaching experiments, >95% of TCIPP was depleted from PUF after 168 h total contact with leaching fluid. Our experiments indicate leaching is potentially a very significant pathway of TCIPP emissions to the environment.

Keywords

Tris (1-chloro-2-propyl) phosphate;
Polyurethane foam;
Landfill;
Chlorinated phosphate flame retardants;
Leaching

1. Introduction

A widely used group of flame retardants are the chlorinated phosphorous flame retardants (PFRs) also known as phosphinates, such as tris(1-chloro-2-propyl)phosphate (TCIPP), tris(2-chloroethyl)phosphate (TCEP) and tris(1,3-dichloroisopropyl)phosphate (TDCIPP). These and other PFRs have been applied to a wide range of commercial products such as: textiles, rubber, polyurethane foam (PUF), cellulose, cotton, electronic equipment cables, casting resins, glues, engineering thermoplastics, epoxy resins, and phenolic resins to meet and comply with fire safety codes, standards and regulations (van der Veen and de Boer, 2012). TCIPP has been found to be resistant to degradation (Leisewitz et al., 2000; Kawagoshi et al., 2002). PFR contamination of indoor air and dust, lakes, river sediment and marine biota across Europe, USA and Japan is well documented (Carlsson et al., 1997; Marklund et al., 2003; Andresen et al., 2004; Björklund et al., 2004; Stapleton et al., 2009; Leonards et al., 2011). Moreover, detection of TCIPP and TCEP in groundwater older than 20 years indicates considerable persistence in aquifers (Regnery et al., 2011). In laboratory experiments, Regnery and Püttmann (2010) demonstrated that TCEP and TCIPP appeared resistant to photodegradation by sunlight. Furthermore, particulate-bound TDCIPP has been shown capable of mid to long-range transport due to its highly persistent nature in the atmosphere with regard to OH radical oxidation (Liu et al., 2014). TCIPP accumulates in the liver and kidneys (Leisewitz et al., 2000), with work by Dishaw et al., (2011) showing it decreases cell number and alters neurodifferentiation. "Skin and eye irritations in animals are unquestioned " (Leisewitz et al., 2000) and is considered potentially carcinogenic (Ni et al., 2007). Concerns over such health impacts are exacerbated by the detection of a metabolite of TCIPP, bis(1-chloro-2-propyl)phosphate (BCIPP) in human urine (Dodson et al. 2014).

Notwithstanding this combination of suspected health effects and demonstrable human exposure, in 2000 the total TCIPP production in Europe was 36,000 tonnes. It is used in applications such as rigid foams in the production of construction blocks and panels used for insulation purposes, and in flexible PUF for soft furnishings and mattresses (EU RAR, 2008). Currently, used furniture polyurethane foams treated with TCIPP are treated as municipal rather than hazardous waste, and are thus landfilled or incinerated. In the UK alone, it is estimated that around 670,000 tonnes of furniture of which a proportion will be PUF was disposed of by householders annually (WRAP, 2012). This reservoir of TCIPP within furniture polyurethane foams has and will continue to gradually enter the waste stream. An EU risk assessment report (EU RAR, 2008) predicts that a typical UK landfill with a leachate flow of $100 \text{ m}^3 \text{ day}^{-1}$ would emit a maximum TCIPP mass via leachate of 6.7 g day^{-1} . There is hence a pressing need to understand the fate of chemicals like TCIPP associated with furniture PUF following disposal. Potential emission pathways for chemicals associated with landfill include contamination of leachate and volatilisation (Stubbings and Harrad, 2014). The physicochemical properties of TCIPP (water solubility = $1,600 \text{ mg L}^{-1}$ at 20°C , vapour pressure = $1.4 \times 10^{-8} \text{ Pa}$ at 21°C and $\text{Log } K_{\text{OW}} = 2.59$ (van der Veen and de Boer, 2012; Tremain, 2002)), suggest that following disposal to landfill such leaching and volatilisation of TCIPP associated with treated PUF may be extensive. TCIPP is an additive chemical not covalently bound to the PUF material and therefore TCIPP escape is relatively facile. Considering that these products are often treated with TCIPP at percent levels by weight (EU RAR, 2008), it is apparent that furniture PUF constitutes a significant potential source of TCIPP to the environment. Despite this, very little research has been undertaken that examines end-of-life management of TCIPP associated with waste soft furnishings (items made of cloth, such

as curtains, chair coverings, etc., used to decorate a room) and furniture. In the absence to our knowledge of empirical data related to the fate of TCIPP treated furniture foam in landfill, this study conducts a series of controlled laboratory experiments to test the hypothesis that TCIPP is capable of leaching from waste furniture PUF.

2. Materials and methods

2.1. Samples

We investigated a flame retardant-treated polyurethane foam sample taken from a sofa cushion. The sample was collected from a sofa prior to entry into the UK waste stream in Birmingham, UK, 2012. As the presence of flame retardants present in the foam was unknown, its chemical content was determined prior to deployment in our leaching experiments. To do so, small pieces of foam (approx. 5 mm × 5 mm × 5 mm) were taken from random points from the sample totalling approximately 50 mg. An accurately weighed aliquot of foam (50 mg) and 5 mL of ethyl acetate were added to a pre-washed test tube, vortexed for 1 min and sonicated for 5 mins before being centrifuged for 2 mins at 2000 rpm. The supernatant was transferred to a clean tube, the extraction was repeated and both supernatants were combined (10 mL total) and vortexed for 1 min. 1 mL of sample was then transferred to a clean tube and diluted using 9 mL ethyl-acetate. Finally 10 μ L of the first dilution was transferred to and diluted further using 90 μ L methanol containing 90 ng d₁₅-labelled TPhP as internal standard (x10,000 dilution in total). The test PUF was analysed via LC-MS/MS (see section 2.4) in quintuplicate.

2.2. Leaching test methods

Four distinct experimental scenarios were undertaken to examine the effects of: (a) contact time (single batch experiments); (b) duration of serial or periodic wetting and draining of waste (serial batch experiments); (c) temperature (20, 50, and 80 °C); and (d) pH level (acidic 5.8, slightly acidic 6.5, and alkaline 8.5) of the leaching fluid on the leachability of the target analyte from the sample material (SI; Table S1). In scenario (a) contact time, the treated sample is contacted once with the leaching fluid for a set predetermined time of either, 6 h, 24 h or 48 h. In scenario (b) serial batch, the sample is contacted with the leaching fluid for 168 h in total, with the resulting leachate being removed from the contact vessel and replenished with fresh leaching fluid 6 times, at intervals of 6 h (batch 1), 24 h (batch 2), 48 h (batch 3), 72 h (batch 4), 96 h (batch 5) and 168 h (batch 6). The leachate was extracted from the contact vessel via pouring or draining through a 0.45 µm pore size glass fibre filter (Advantec, Japan), in which the contact vessel was inverted for approximately 5 mins to ensure as much leachate was removed as possible. Each batch of leachate were analysed for analyte concentrations at the given intervals. Leaching fluids were prepared as previously described in Stubbings and Harrad, 2016. PTFE bottles (500 mL) were used as contact vessels during controlled leaching experiments. The contact vessel was not completely filled with leaching fluid and as a result headspace was present inside the contact vessel. In all experiments, 1 g of PUF sample was contacted with 100 mL of Milli-Q water giving a liquid-solid ratio of 100:1 (v/w). Following addition of the sample and leaching fluid, contact vessels were horizontally agitated on a mechanical shaker at 200 rpm for the desired contact time. In scenario (c) samples examining the influence of temperature, the contact vessels were not agitated and instead were submerged in a water bath for 24 h at the

desired temperature. In scenario (d) experiments were agitated at 200 rpm for 6 h and the initial pH of the leaching fluid before contact with flame retarded PUF samples was recorded. Each of the above leaching experiments were conducted in duplicate.

2.3. Sample preparation and chemical analysis

Each leachate sample was filtered through a 0.50 μm size particle retention glass fibre filter (Advantec, Japan) to remove any textile fibres from the leachate and then spiked with 10 μg of d_{15} -labelled Tri-phenyl-phosphate (TPhP) as internal (or surrogate) standard. The filtrate was then extracted in series using 2 x 50 mL dichloromethane (DCM) by liquid-liquid extraction with mechanical shaking for 30 mins each time. Approximately 5-10 mL 2% NaCl solution was used to enhance separation after extraction. The combined DCM extracts were dried via filtration through Na_2SO_4 . The dried extract was concentrated to 0.5 mL using a Zymark Turbovap II with solvent exchange to *n*-hexane before being loaded on to a 2 g pre-cleaned, activated florisil column and washed with 20 mL *n*-hexane. The TCIPP was then eluted using 20 mL ethyl acetate. The eluate was evaporated to incipient dryness and then reconstituted to 100 μL with addition of 25 ng d_{27} -labelled TnBP as a recovery standard in methanol. Prior to analysis via LC-ESI-MS/MS the samples underwent further dilution in which a 10 μL aliquot was taken and diluted with 990 μL of methanol, and then an additional 10 μL aliquot of that first 1 mL dilution was taken and diluted with 990 μL of methanol to yield a 10,000 times dilution. This was necessary due to the very high concentrations of TCIPP in samples.

2.4 Determination of concentrations of TCIPP

Concentrations of TCIPP in all samples generated in experiments were using a dual pump Shimadzu LC-20AB Prominence high pressure liquid chromatograph (Shimadzu, Kyoto, Japan) equipped with a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) (see SI for additional details).

2.5. Calculation of TCIPP leaching

The percentage of TCIPP present in PUF that was leached into each leachate sample (PL) was calculated as previously defined by Stubbings and Harrad, (2016) (equation 1):

$$\text{Equation 1: } PL = \left[\frac{C_{leachate} \times V}{C_{waste} \times W} \right] \times 100\%$$

PL = percentage leached (%)

$C_{leachate}$ = Concentration of TCIPP in leachate (mg/L)

V = volume of leachate (L)

C_{waste} = Concentration of TCIPP in PUF (mg/kg)

W = weight of PUF sample subjected to leaching (kg)

The percentage of TCIPP leached normalised to contact time (PLT , % h^{-1}) is calculated according to equation 2.

172 Equation 2: $PLT = \frac{PL}{t}$

173 PL = percentage leached (%)

174 t = contact time (h)

175

176 **2.3. Data analysis**

177 Basic and descriptive statistics were calculated using IBM SPSS Statistics 24, and Microsoft

178 Excel 2013 software. Plots were generated by Microsoft Excel 2013.

179

180 **3. Results and discussion**

181 **3.1. Initial TCIPP concentrations in the furniture PUF samples**

182 The average \pm standard deviation concentration of TCIPP determined in five 50 mg sub-

183 samples of the PUF sample used in this study was $17,000 \pm 13 \text{ mg kg}^{-1}$ or 1.7% by weight.

184 This is consistent with information provided to the authors that TCIPP is typically added to

185 flexible PUF at 1-4% by weight (pers. comm. Flexible Foam Research Ltd, 2014).

186

187 **3.2. Effects of contact time on TCIPP leaching from single batch experiments.**

188 TCIPP concentrations in leachate (mg L^{-1}), as well as mean PL (%) and mean PLT values ($\% \text{ h}^{-1}$)

189 ¹) generated from the single batch experiments are provided in Table 1. There were no

190 significant ($p > 0.05$) differences in TCIPP concentrations in leachate generated via different

contact times. This suggests that contact time has comparatively little effect on TCIPP leaching from furniture PUF, therefore leaching from the PUF material appears to occur in the early stages of contact with the leaching fluid. The quantity of TCIPP being leached in experiments exceeds substantially that observed for polybrominated diphenyl ethers (PBDEs) from cathode ray tube (CRT) plastic housing (Stubbings and Harrad, 2016).

3.3. Effect of cyclical wetting and draining on TCIPP leaching (serial batch experiments)

Average concentrations of TCIPP (mg L^{-1}) detected in leachate and mean *PLT* values ($\% \text{ h}^{-1}$) obtained from the serial batch experiments are presented in Figure 1, with TCIPP concentrations, mean *PL* (%) and mean *PLT* values ($\% \text{ h}^{-1}$) for the same experiments provided in SI (Table S6). After 6 h contact time, concentrations of TCIPP leached from flexible PUF in these serial batch experiments diminish with increasing experimental duration. However, the extent of TCIPP leaching from the material is substantial, and after a cumulative 168 h of leaching, the cumulative total of TCIPP removed from the furniture foam by the leaching fluids approaches 96% of the initial mass present in the PUF sample (Figure 2). Overall – although longer term experiments are required to confirm this - this serial batch experiment indicates that replenishment of leaching fluid as would be expected in a landfill could result in the near-total removal of TCIPP from PUF via leaching over long periods.

3.4. Leaching kinetics

Ho et al., (2005) expressed the leaching of water-soluble components from sapwood in terms of the following second-order rate equation:

Equation 3:
$$\frac{Ct}{t} = k(Cs - Ct)^2,$$

where k is the second-order leaching rate constant ($\text{L ng}^{-1} \text{min}^{-1}$), C_s the leaching capacity, which is the concentration of TCIPP at saturation (ng L^{-1}), and C_t is the concentration of TCIPP (mg L^{-1}) in suspension at any given time, t (min). The leaching capacity, C_s , and the second-order leaching rate constant, k , can be determined experimentally from the slope and intercept by plotting t/C_t against t .

Plots were generated to evaluate whether TCIPP leaching from PUF could be explained using second order leaching kinetics. In contrast to the analogous experiments with PBDEs leaching from CRT plastic chips (Stubbings and Harrad, 2016) and hexabromocyclododecane (HBCDDs) from textiles (Stubbings et al, 2016), the concentrations of TCIPP in leachates from serial batch experiments were not included in generating these plots because the greater removal of TCIPP from the foam resulted in significantly lower initial concentrations in the PUF between batches. Therefore, only duplicate measured leachate concentrations in single batch experiments conducted at 20 °C for each contact time (6 h, 24 h and 48 h) and also for each DHM concentration were included in leaching kinetics calculations. Using the equations described in Stubbings et al. (2016), t/C_t was plotted against t , where C_t is the concentration of TCIPP (mg L^{-1}) in suspension at any given time and t (min). The resulting plots are provided for DHM concentrations 0, 100 and 1,000 mg kg^{-1} in the SI (Figure S2), and show that the y-intercept and therefore k values are negative for each DHM

concentration. These data suggest that TCIPP leaching from PUF is not a second order kinetic process.

To evaluate if the leaching of TCIPP from PUF is governed by first-order kinetics, we plotted the natural logarithm of TCIPP concentration versus time (Figure 3). We generated such plots for all single batch experiments conducted at 20 °C and for each DHM concentration. The plots are linear with a negative slope in all instances; suggesting that leaching of TCIPP from PUF may be a first-order process. A caveat is that these conclusions are based on only 6 data points per plot (duplicates at 3 contact times). Moreover, only the plot for the experiments where the leaching fluid contained 100 mg L⁻¹ DHM was significantly linear ($p < 0.05$). However, the leaching fluid containing 0 mg L⁻¹ DHM was significant at a lower confidence interval ($p < 0.10$). The slope, Y-intercept, the leaching rate constant, k (min⁻¹), two-tailed p values, and Pearson's correlation coefficients, r , for these 1st order plots are given in Table 2.

We offer here some possible explanations for why TCIPP does not fit with second order kinetics as has been observed for HBCDD and PBDEs from fabrics and CRT plastic housing chips (Stubbings et al. 2016; Stubbings and Harrad, 2016). Firstly, PUF is more porous, permeable and has a larger surface area than other materials tested. This allows the leaching fluid to access far greater surface area than in less porous materials. Secondly, there are significant differences in the physicochemical properties between the chlorinated phosphates and the brominated flame retardants, with TCIPP possessing an aqueous solubility 20,000 – 800,000 times greater than PBDEs.

3.5. Effects of temperature on TCIPP leaching from furniture PUF samples.

Within a landfill, temperatures can sometimes reach as high as 80-90 °C due to heat released during aerobic degradation (Kjeldsen et al., 2002). Therefore, the influence on *PLT* of leachate temperatures of 20 °C, 50 °C and 80 °C were investigated. Leachate concentrations for TCIPP from flexible PUF at different temperatures and DHM concentrations are displayed in Figure 4. TCIPP concentrations, mean PL (%) and mean *PLT* values (% h⁻¹) in these experiments (conducted in duplicate) are provided in SI (Table S7).

There are significant differences in TCIPP concentrations in the leachate between 50 °C and 80 °C for both DHM containing leaching fluids, while the differences between these temperatures are significant at a lower confidence interval ($p = 0.059$) for deionised Milli-Q leaching fluid. There is also a significant ($p = 0.057$) difference between TCIPP concentrations in leachate generated at 20 °C and 50 °C when the leaching fluid was deionised water. The lower TCIPP concentrations present in leachates at 80 °C relative to those at 50 °C may be a result of enhanced TCIPP volatilisation at this higher temperature as well as TCIPP potentially entering the headspace of the leaching vessel in the gas phase and being lost when the vessel was subsequently opened.

3.6. Effects of pH on TCIPP leaching from furniture PUF.

The influence of leachate pH values of 5.8, 6.5 and 8.5, on TCIPP leaching behaviour was investigated. Leachate concentrations values for TCIPP from flexible PUF at different pH values and DHM concentrations are displayed in Figure 5. Duplicate TCIPP concentrations,

mean PL (%) and mean *PLT* values (% h⁻¹) for the same experiments are provided in the SI (Table S8).

In leachates to which no DHM was added there were significant differences ($p < 0.05$) in TCIPP concentrations between pH 5.8 and 8.5, and 6.5 and 8.5. In leachates in which 100 mg L⁻¹ DHM was present, there were no significant differences in TCIPP concentrations between the pH values studied. At 1,000 mg L⁻¹ there are significant differences between pH 5.8 and 8.5, and 6.5 and 8.5. The alkaline pH of 8.5 generated the highest concentrations of TCIPP in the leachate for all three DHM concentrations explored. Generally, more alkaline leaching fluids remove more TCIPP from the foam.

3.7. Effects of agitation on TCIPP leaching from furniture PUF

By comparing the results of experiments conducted at 20 °C using Milli-Q water with contact times of 24 h with and without agitation, the effect of agitation on TCIPP leaching from the PUF can be examined (SI; Figure S4). The results of a paired sample t-test are presented in SI (Table S9) and indicate that there are significant differences ($p < 0.05$) in TCIPP concentrations between agitated and non-agitated samples. The effect of agitation on treated PUF is to enhance TCIPP leaching across all three DHM concentrations examined; concentrations of TCIPP in agitated samples were on average 43% higher at 0 mg L⁻¹ DHM, 14% greater at 100 mg L⁻¹ DHM, and were elevated by 32% at 1,000 mg L⁻¹ DHM.

3.8. Statistical analysis of the whole data set

The results of multiple linear regression analysis (MLRA) for TCIPP treated flexible PUF are provided in the SI (Table S10). The importance value ranks the effects of the independent variables from greatest to smallest. Of the independent variables explored in these experiments, the pH of the leaching fluid had the greatest effect on TCIPP concentrations. The alkaline pH of 8.5 yielded the greatest TCIPP concentrations in leachate. The contact time was significantly negatively correlated with TCIPP concentrations in leachate. This may be due to greater degradation of TCIPP at longer contact times, but is more likely driven by the inclusion of the serial batch experiments in the MLRA, in which concentrations of TCIPP in the PUF were heavily depleted in subsequent batches, thereby yielding lower concentrations at longer contact times. The DHM content of the leaching fluid was also shown to exert a significant influence on TCIPP leaching from PUF, with higher DHM concentrations leading to greater TCIPP concentrations in leachate. Finally, the effect of leaching fluid temperature on TCIPP concentrations in leachate is not significant – presumably the increased solubility of TCIPP at higher temperatures was offset by some other factor, such as the aforementioned potential entry of TCIPP into the headspace of the leaching vessel with subsequent loss on opening the vessel.

4. Summary

We present evidence that under laboratory conditions, leaching of TCIPP from furniture PUF is extensive, occurs rapidly and appears to be a first order kinetic process. This suggests that TCIPP in furniture foams disposed of at landfill is likely to readily leach into percolating waters and that very substantial releases to leachate from such discarded foams are likely.

Given the widespread use of TCIPP in furniture foam, this study suggests that greater knowledge of its presence and of other PFRs in landfill leachate is urgently required. More research is required to ascertain how much TCIPP and other PFRs are removed at WWTPs receiving landfill leachate in the UK by measuring effluent flows. It would also be of benefit to measure the quantity of PFRs in influent flows, to calculate removal efficiencies. Moreover, the potential for contamination of groundwater and drinking water with PFRs should be explored.

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Table 1: Concentrations (mg L^{-1}) of TCIPP in leachate in duplicate experiments, together with mean PL (%) and mean PLT values ($\% \text{ h}^{-1}$) derived from contacting PUF with artificial leachate.

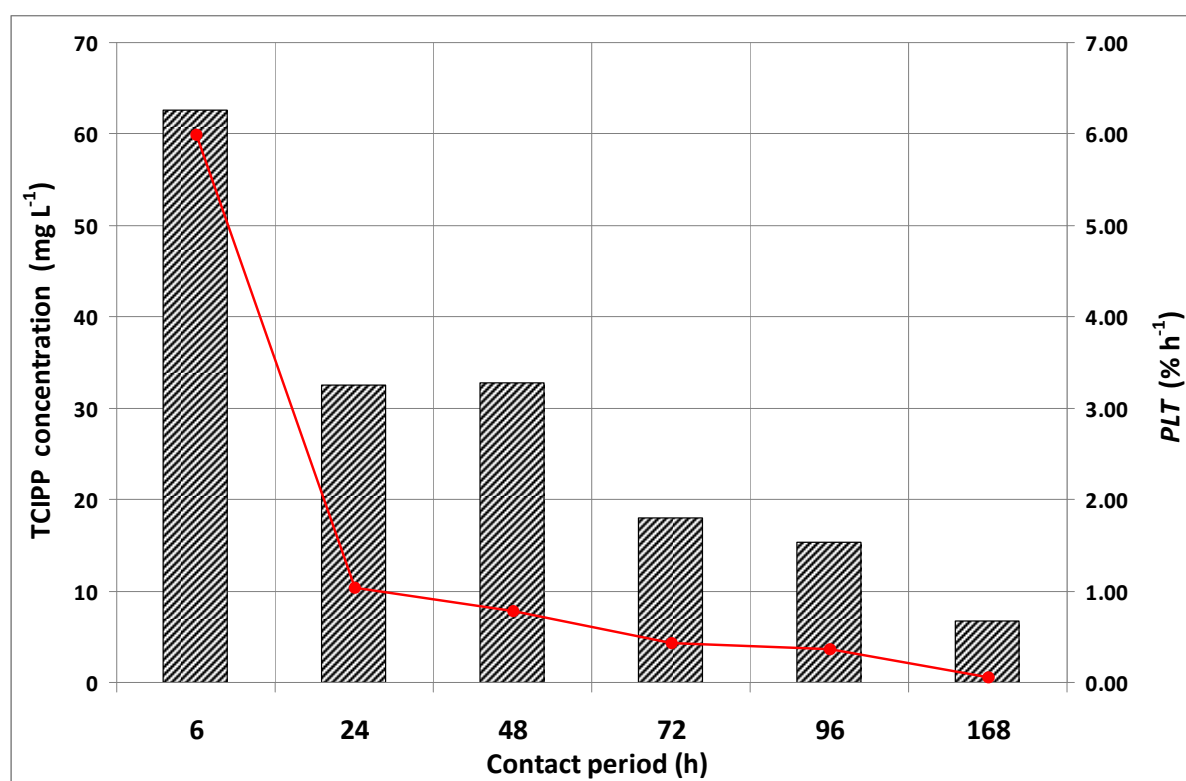
DHM conc. (mg L^{-1})	Contact time (h)	TCIPP Conc. (mg L^{-1})	TCIPP Conc. (mg L^{-1})	PL (%)	PLT ($\% \text{ h}^{-1}$)
0	6	59	67	36	6.0
0	24	29	22	15	0.61
0	48	16	36	15	0.31
100	6	60	67	36	6.0
100	24	61	68	37	1.6
100	48	49	47	28	0.58
1,000	6	70	69	40	6.7
1,000	24	89	63	44	1.8
1,000	48	45	68	33	0.68

DHM: dissolved humic matter; PL: percentage leached; PLT: percentage leached normalised to contact time.

Table 2: First order leaching rate slopes, y-intercepts, constants (k), and r values obtained from experiments examining the leaching of TCIPP from PUF.

Constant / DHM Conc. (mg L ⁻¹)	Slope (log _e mg L ⁻¹ /min)	y-intercept (log _e mg L ⁻¹)	k (min ⁻¹)	Two-tailed p value	Correlation coefficient: r
0	-0.0004	4.1	0.000000031	.095	-0.737
100	-0.0001	4.2	0.000000030	.044	-0.824
1,000	-0.0001	4.3	0.000000022	.316	-0.497

422



423

424 **Figure 1: Mean (n=2) TCIPP concentrations (mg L⁻¹; bars) and *PLT* (% h⁻¹) (red circles) in**
 425 **leachate produced by experiments examining the effect of cyclical wetting and draining**
 426 **(serial batch) on TCIPP leaching from PUF.**

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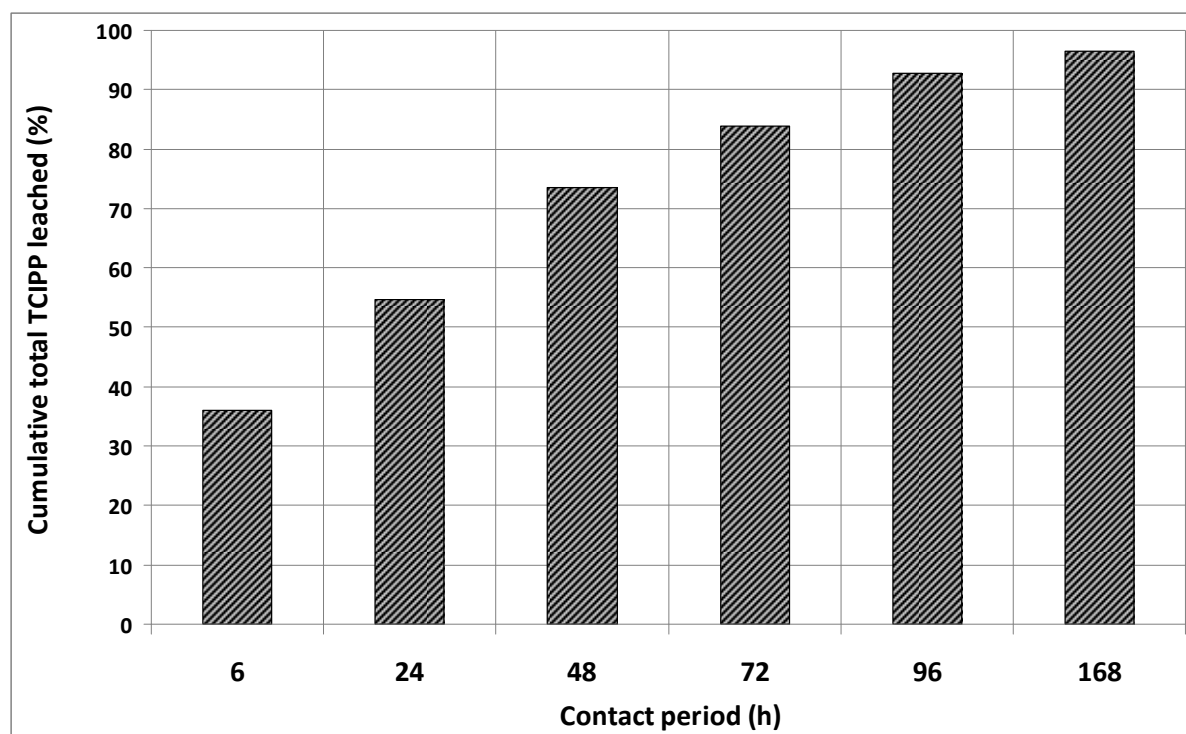
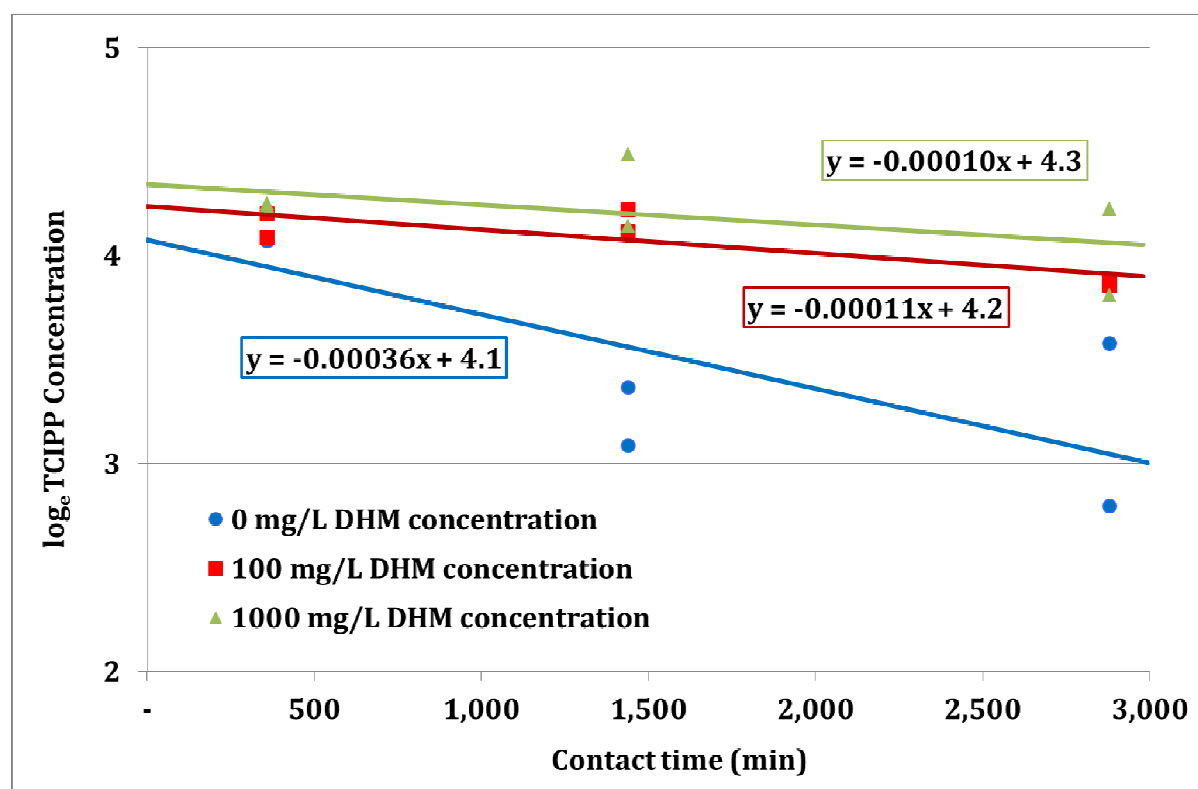


Figure 2: Cumulative total TCIPP leached (% present in source PUF) during experiments examining the effect of cyclical wetting and draining (serial batch) on TCIPP leaching from PUF.

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436 **Figure 3: Plot of natural logarithm of concentration of TCIPP in leachate versus time (t ,**
 437 **min) in single batch experiments examining TCIPP leaching from PUF.**

438

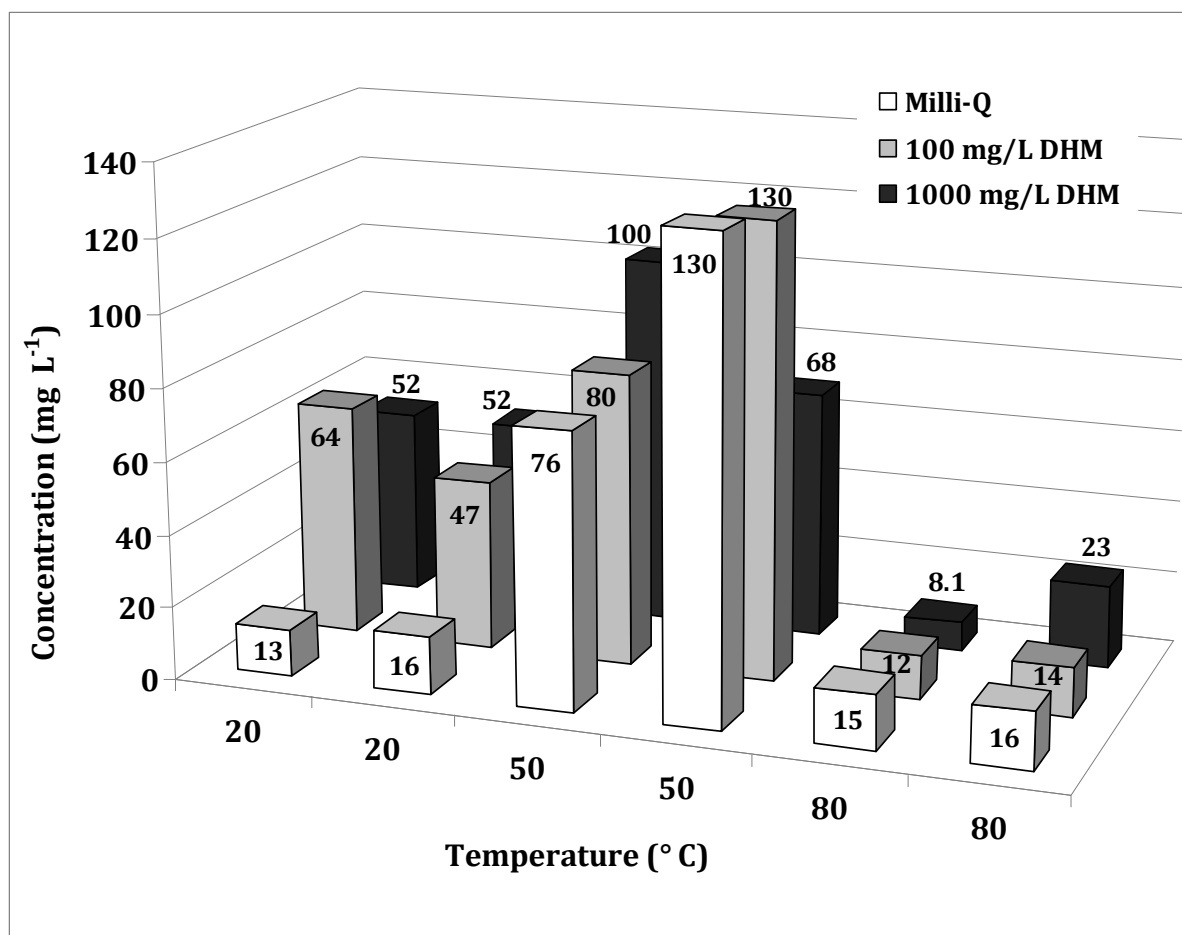
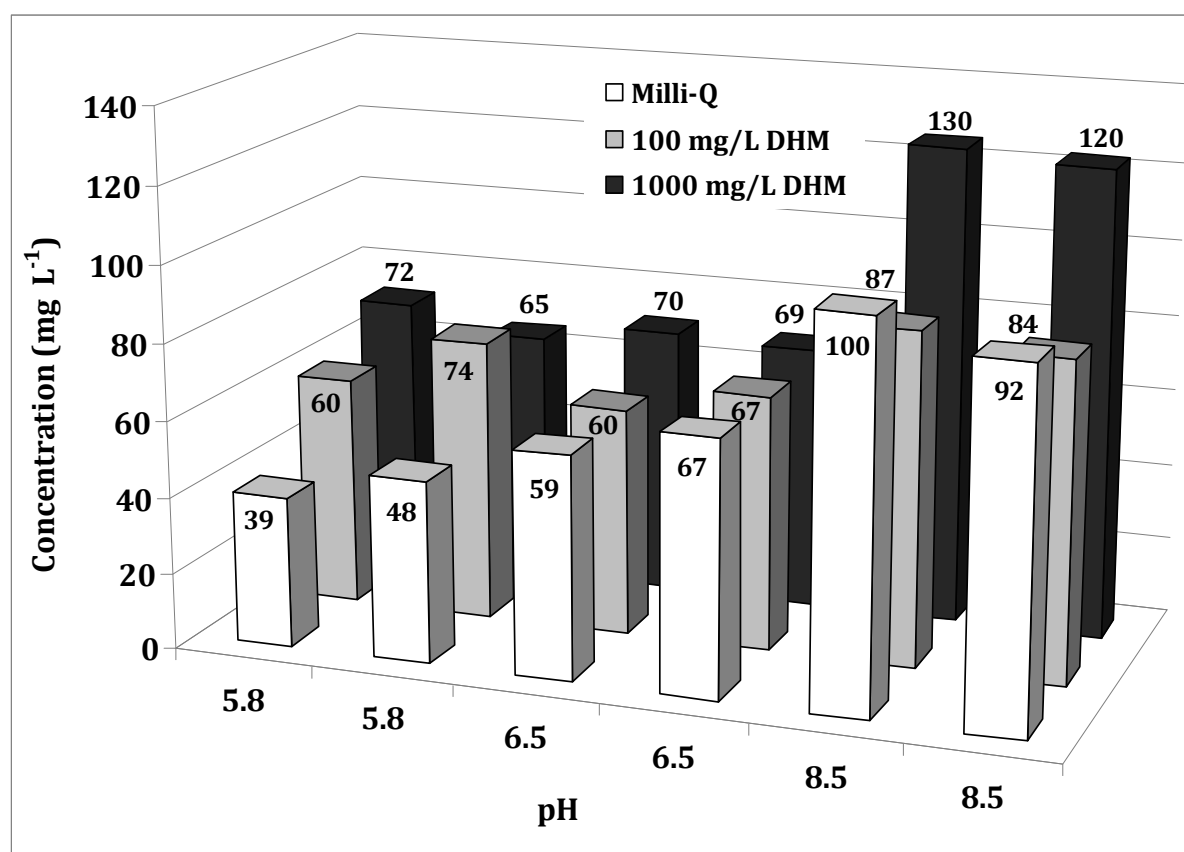


Figure 4: TCIPP concentrations (mg L⁻¹) in leachate produced during 24 h single batch experiments (run in duplicate) examining TCIPP leaching from PUF at different temperatures and DHM concentrations in leaching fluid. Data labels on bars are rounded to two significant figures.

446



447

448 **Figure 5: TCIPP concentrations (mg L⁻¹) in leachate produced during single batch**
 449 **experiments examining TCIPP leaching from PUF at different pH values and DHM**
 450 **concentrations in leaching fluids. Data labels on bars are rounded to two significant**
 451 **figures.**

452

Highlights

- We study TCIPP leaching from furniture polyurethane foam (PUF)
- Leaching of TCIPP from PUF appears to be a first order process
- In serial batch leaching tests, >95 % of TCIPP was depleted from PUF after 168 h
- TCIPP concentrations between 13 mg L^{-1} – 130 mg L^{-1} were detected in the leachate
- leaching is potentially a significant pathway of environmental TCIPP emissions